

# Order for order-disorder?

***There seems to be a simple rule for telling when some semiconducting ternary alloys have an order-disorder transition below the melting point. Will it apply to potentially commercial semiconductors?***

CHEMISTRY at its most appealing is applied common sense. This is the spirit in which people in the nineteenth century were able to devise empirically based rules relating properties of one kind to those of another for some class of chemicals. Sometimes the outcome would be simply a useful way of codifying data and of making plausible predictions, as in the empirical statement that the entropy of vaporization at the boiling point is roughly constant, called Trouton's rule. But in the early decades of the century, much bigger prizes had been won from these empirical relationships. Would there have been an atomic theory in Dalton's time without the law of multiple proportions, for example?

So it is good that the tradition still flourishes, even in unlikely connections. Thus Alex Zunger, from the Solar Energy Research Institute at Golden, Colorado, has just applied exactly such a technique to the codification of order-disorder transitions in the three-component alloys on which those who design new semiconductors have set their hearts (*Appl. Phys. Lett.* 50,164; 1987).

The importance of the problem is evident. Sooner or later, no doubt, silicon will be replaced by materials such as gallium arsenide (GaAs) or indium antimonide (InSb) in the microcircuits on which we all rely. The principle, which explains why chemists are closely engaged with these developments, is simply that if, say, germanium is a semiconductor, an alloy of the two elements on either side of it in the Periodic Table, Ga and As, will almost certainly be a semiconductor as well. Experiment indeed confirms that the outer-shell electrons of Group III gallium and Group V arsenic fill the valence band of an equi-atomic alloy, but leave the conduction band essentially empty.

For the past decade, chemists have been busily ringing the changes on this and other recipes for making semiconductors, knowing how great the practical benefits could be. GaAs should be faster than silicon, while sandwiching an alloy in which 30 per cent of the Ga atoms are replaced by Al (also in Group III) between slices of GaAs will make an infrared laser as well. The practical snag is the difficulty of controlling the stoichiometric balance of the composition to a few parts in 100 million, the level at which electronic doping by foreign ingredients can be significant.

Zunger is concerned with a lesser but still important snag — the circumstance

that semiconductors that are ternary compounds should in principle exist in one or other of two alternative states, ordered and disordered. In the case of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ , for example, where Al and Ga are electronic substitutes for each other and where the electronegativity of the As is likely to give it anionic properties and thus large size (relative to the Al and Ga atoms in the lattice), it is an interesting but open question whether the Al and Ga atoms are distributed randomly and, if not, whether they are ordered in clusters or in some other way. Moreover, the electronic properties of the material could depend on what the answer is. The transition from order to disorder should decrease the band-gap, for example.

Luckily, most semiconductors appear to be built on the architecture of the diamond lattice — that of a tetrahedron in which an anionic atom is surrounded by four cationic atoms (and, for that matter, vice versa), which allows Zunger plausibly to compare semiconductors whose order-disorder transitions are likely to occur at low temperatures where they cannot easily be observed with those of other materials where the transition has actually been observed. Specifically, he considers the range of ternary alloys or molecular compounds in which two electronegative Group V or VI atoms are combined respectively with one Group I and one Group IV atom or with one Group II atom and one from Group V.  $\text{AgInTe}_2$  might stand for the first class of compounds  $\text{ZnSiAs}_2$  for the second. The materials are respectively chalcopyrites and pnictides. Zunger lists more than 30 known semiconductors of both kinds.

These materials differ from those at the centre of the device-makers' attention in that the cationic components, not being isovalent, are far from being electronic substitutes for each other, as Ga and Al are. Zunger points to two energetic consequences of this state of affairs for the order-disorder problem.

First, the ordered state in which each anionic atom (from group V or group VI) is surrounded tetrahedrally by two pairs of cationic atoms is likely to persist to much higher temperatures than in alloys in which, say, Ga and Al atoms may substitute for each other with negligible energetic penalty. This is what the experiments show: order-disorder transitions have been observed in 13 out of the 30-odd chalcopyrite semiconductors at tempera-

tures not far short of the melting point (about 1,000 °C.) The snag, for materials such as  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ , is that the energetic differences between the cationic components are so small that the transition, if it occurs, will be at too low a temperature for it to be practicable to tell whether the usually disordered state of the alloy is the lowest or merely a metastable state.

Zunger's second observation is where the common sense comes in. If there are low-temperature ordered states in ternary alloys of this kind, they will not be tetrahedrally symmetric about the cations, but distorted so as best to accommodate the two different ionic radii of the two pairs of cations. The disordered state, on the other hand, in which cations are distributed at random about their central anions, must be tetrahedrally symmetric, which means that the lattice embodies a substantial penalty in internal energy (or in enthalpy) in exchange for the benefits of the extra entropy that comes from the disorder.

What Zunger does is what chemists have been doing for two centuries. He defines a parameter (called  $u$ ) to represent the measured departure from tetrahedral symmetry in the ordered phases of the chalcopyrite alloys. (Numerically,  $u$  is determined by the difference, in the ordered phase, between the distances from the central anion to each of the two different kinds of cations.) Intuitively, one would expect that if there are ternary alloys that make a transition from order to disorder before they melt they will be the alloys for which the value of  $u$  is the smaller.

This, magically, is how it turns out. For the 23 compounds for which data exist, the 13 that make a transition to disorder before melting have  $u$  less than 0.265; the remaining ten, which remain ordered up to the melting point, have larger values of  $u$ . Emboldened by the fact that there are no known exceptions to his rule, Zunger goes on to predict which side of the fence ten compounds not yet made will fall.

There are several lessons to be learned from this elegant exercise. The argument that lattice strain may stabilize order may be extended to alloys of more immediate interest. It may even be possible to make a numerical connection between disorder and the reduction of the semiconductor band-gap it brings about. But the chief may be that there is mileage yet in a style of argument that seemed to go out of fashion when people took to chemistry by supercomputer.

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